A Circular Economy Approach to Plastic Waste

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Abstract: Growing environmental concerns associated with the accumulation of plastic waste in the natural environment has incentivised considerable research into renewable alternatives, and more recently, alternative waste management strategies. This review aims to introduce polylactide (PLA), a bioplastic, and recent research within the field. Attention will then shift to research surrounding plastic waste management. Various end-of-life (EOL) options available to plastics will be discussed more broadly, before presenting existing technologies, challenges and future opportunities exclusively for PLA. Herein, all waste management strategies presented for PLA are discussed within the context of industrial feasibility.

Key Words: Polylactide, circular economy, end-of-life, catalysis

1.0 Introduction

Polymers (plastics) have played an instrumental role in the development of modern society. Indeed ubiquitous, owing to their superior material properties and affordability, polymers have found use in a variety of different sectors, from packaging and construction through to electronics and agriculture, to name but a few.[1] Global polymer production annually exceeds 300 million tonnes, consuming *ca.* 6% of oil produced globally, which is anticipated to rise to 20% by 2050.[2–5] Alarmingly, whilst petroleum-based products dominate the industry, *ca.* 99% in 2015, it is clear polymer production based on depleting fossil fuel reserves is unsustainable.[6] Moreover, growing environmental and geopolitical pressures associated with resource extraction and production serve to further incentivise change.[1,7–9] To remedy such concerns, the biopolymer industry has emerged as a promising solution, utilising an alternative feedstock, namely biomass. [4]

1.1 Biomass

As society pursues a low-carbon future to mitigate growing environmental concerns, it is imperative the industry proactively shifts from petrochemical feedstocks, with biomass emerging as the outstanding candidate.[4] Biomass is a renewable resource comprising of lignin, proteins, oils and carbohydrates, sourced from plants, crops and field residues, to name but a few.[4,10] Polysaccharides (sugars) represent a particularly promising feedstock, with production amounting to 150 billion tonnes per year.[4] However, human consumption amounts to only 1% by volume, alleviating any concerns associated with food chain competition.[4] Whilst the biopolymer industry remains very much in its infancy, accounting for just 1% of all processed plastics globally, the promise of this relatively untapped, abundant resource has stimulated considerable growth, exemplified by production increasing from 300,000 to 2.1 million tonnes between 2009-2018.[2,10] Current barriers to biopolymers include cost, which are typically higher compared to petrochemically derived polymers.[11] Biopolymers are, however, expected to become more prominent due to increasing public awareness, legislative drives and increasing oil prices.

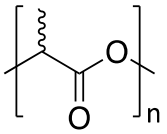
1.2 Biopolymers

A biopolymer can be defined as a polymer that is either bio-based, biodegradable or both.[2] However, it is important to highlight that whilst this term is synonymous with renewable polymers, this is not to say they are inherently biodegradable.[2,12] Indeed, biodegradability is not limited to bio-based polymers, with some polymers based on traditional petrochemical feedstocks also exhibiting this environmentally attractive property, for example Poly(caprolactone) (PCL).[13,14] Furthermore, biopolymers can be categorised into three distinct classes: 1. Natural polymers, 2. Polymers derived from microbial fermentation and 3. Synthetic polymers based on naturally occurring

monomers.[1,10,13] The focus of this perspective will be on the latter class, namely poly(lactic acid), (PLA).[6,10,13,15–19]

2.0 PLA

Ever increasing environmental pressures, in conjunction with depleting fossil fuel reserves, have played a crucial role in incentivising polymer research into renewable alternatives, with PLA emerging as one of the most promising candidates within the last 20 years.[15] PLA is a renewable aliphatic polyester based on a repeating lactic acid (LA) monomer unit (Figure 1).



PLA

Fig 1. Polymeric structure of PLA.

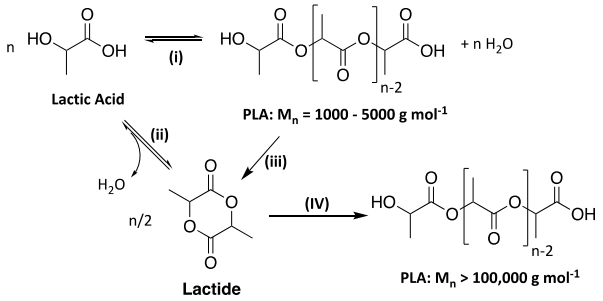
PLA has been extensively researched in the literature, owing to its favourable environmentally benign qualities and biodegradability.[6,15–18] As such, PLA has found use in a variety of different sectors, most notably in packaging for short shelf-life products, including food and beverages. [6,10,15–19] Additionally, since PLA is derived from a naturally occurring product, lactic acid, it is inherently biocompatible, and thus has consequently been exploited in the biomedical industry. Common examples in the field include use in drug delivery systems, implants and tissue scaffolds.[6,19,20] However, to date, PLA has been primarily limited to single-use, disposable applications, owing to its intrinsic brittleness, poor heat resistance and hydrolytic instability. It is also worth noting such properties are dependent on the final polymers *D*/*L*-isomer composition, with the resulting stereocomplex having a higher melting temperature compared to neat PLLA or PDLA. [6,8,10,19,20]

2.1 Synthesis

Production of LA. Lactic acid is principally derived from feedstocks rich in starch, such as corn and sugar. Homolactic bacteria are then deployed to retrieve lactic acid *via* the microbial fermentation of *D*-glucose, which is naturally produced in such feedstocks.[16] Commercial scale production of lactic acid involves using a large-scale batch fermentation reactor operating at high lactic acid concentration to achieve optimal process efficiency, typically taking between 3-6 days.[21–23] However, process conditions below optimum are often conceded in order to preserve optimal activity of the bacteria, thus a neutral pH is maintained through the addition of either $Ca(OH)_2$ or $CaCO_3$. Consequently, calcium lactate is formed, which is then crystallised prior to acidification using H_2SO_4 from which crude lactic acid is then isolated.[22–24] NatureWorks LLC have disclosed the life cycle inventory for the their

PLA production, detailing the energy and material inputs for the industrial fermentation of lactic acid.[25] Synthetic routes using zeolites have also been reported in the literature, with size exclusion preventing both racemisation and undesired side product formation. However, such technology remains limited to the lab-scale at present. [26]

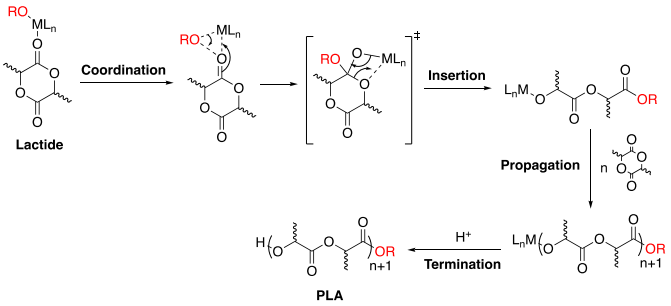
Polycondensation of Lactic Acid. Industrial scale production of PLA traditionally relies on the polycondensation of lactic acid in a step-growth polymerisation reaction.[27] However, this process is limited to producing PLA of low number average molecular weight (M_n), typically between 1000-5000 g mol^{-1}, arising due to poor control. Both the liberation of H_2O and formation of six-membered ring by-products, through the condensation of lactic acid starting material, contribute to the poor M_n obtained, which is reflected in a low degree of polymerisation (DP). To combat this, chain-coupling agents, such as acid chlorides/anhydrides, are often employed to produce PLA of sufficient M_n, possessing material properties suitable for industrial application, at the expense of increased manufacturing cost and complexity. [22,27,28] The polymerisation reaction depicted in Scheme 1 (i and ii) is an example of an equilibrium process, namely esterification. Thus, high PLA conversion can be achieved through the use of higher operating temperatures and reduced pressures, which promote the removal of H_2O, thus shifting the equilibrium in favour of the polymer product. In light of this challenge, research has been incentivised by the need to develop less energy demanding synthesis routes and potentially stereoselective processes, for example the depolymerisation of low M_n PLA to lactide (Scheme 1, iii), followed by the ring opening polymerisation mechanism (Scheme 1, IV).[15,19,22,29]



Scheme 1. Synthesis route for high M_n PLA, adapted from [22].

Ring Opening Polymerisation (ROP) of Lactide. Having first been employed in the pioneering work by Carothers *et al.*[30] in the 1930s, the ROP of lactide (Scheme 1, IV) enables PLA of high and well-defined M_n to be produced, and thus is the industrially preferred method.[6,15,19,22] Whilst polymerisation is an intrinsically entropically unfavourable process ($\Delta S_{ROP\ of\ Lactide} = -41.1$ J K^{-1} mol^{-1}), the ring-strain relief provided by the ring opening serves as the thermodynamic driving force for the process ($\Delta H_{ROP\ of\ Lactide} = -23.0$ kJ mol^{-1}).[31] A number of ROP pathways have been reported in the literature, including anionic and cationic lactide polymerisation, but this perspective will discuss only the most widely considered synthetically useful method in the ROP of lactide, namely coordination-

insertion, as seen in Scheme 2.[15,19,21,22] Initially, the carbonyl carbon on the lactide fragment is activated by coordination to a Lewis acidic metal centre (M) bearing an alkoxide ligand (OR), which subsequently inserts, generating a four-membered ring intermediate. Subsequent insertion is initiated through cleavage of the acyl bond, forming a new metal alkoxide bond. Propagation ensues until a proton source is added to terminate the polymerisation reaction. As seen in Scheme 2, it is evident the growing polymer chain in the ROP mechanism is characterised by two distinctive terminal functional groups: 1. An ester group generated from the alkoxide insertion step and 2. A hydroxyl group, with hydrolysis of the terminal M-O bond achieved through post polymer acid work-up.[21]



Scheme 2. Coordination-insertion mechanism for the ROP of Lactide, adapted from [21]. H^+ corresponds to a proton source, such as an acid, alcohol or H_2O.

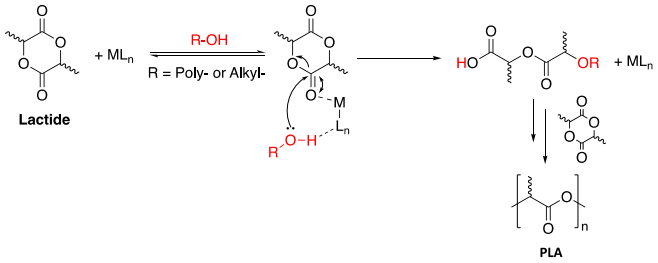
This metal-mediated coordination-insertion mechanism has been subject to considerable commercial interest, owing to its ability to produce PLA of high and well-defined M_n (> 100,000 g mol^{-1}).[6] Additionally, whilst anionic and cationic lactide polymerisation are traditionally conducted under solvent conditions, coordination-insertion (Scheme 2) can be conducted in the monomer melt, removing the need for potentially expensive and environmentally harmful solvents.[32] Alternatively, the ROP of lactide can also proceed *via* an activated monomer mechanism (Scheme 3), arising when a coordinatively saturated metal complex (ML_n) is employed, often requiring a co-initiator, such as an alcohol, owing to the absence of a labile group on the metal centre for insertion.[33] Metal- free ROP of lactide can also be achieved with monomer activation through interaction with an organocatalyst.[34–38] Exotic and functionally diverse PLA architectures can be accessed through manipulation of the initiating system employed,[6,33,39] but such chemistry falls beyond the scope of this review, and therefore will not be discussed. The aforementioned ROP mechanisms represent the most commercially attractive methods for PLA synthesis, especially coordination-insertion, and thus are typically the method of choice in the literature.

2.2 Stereocontrol

Stereoisomerism of Lactic Acid and Lactide. Lactic acid possesses two optically active enantiomers, namely *L* (-) and *D* (+) (Figure 2, i). Consequently, lactide exhibits three distinct configurations: *L-, D-*

and meso-lactide (Figure 2, ii). Commercially, lactide is available either as the *L*- stereoisomer, or alternatively as a racemic mixture, consisting of a 50:50 composition of the *L- and D-* isomers; *rac*-lactide.

PLA Tacticity. The tacticity along the PLA backbone is dependent on both the stereochemistry and order of insertion of the monomer precursor, which can have significant effects on the material properties exhibited by the final polymer.[16,29,40] Intuitively a number of different polymeric tacticities can be accessed through the polymerisation of lactide (Figure 3).



Scheme 3. Activated monomer mechanism in the presence of a co-initiator, commonly an alcohol. Adapted from [33].

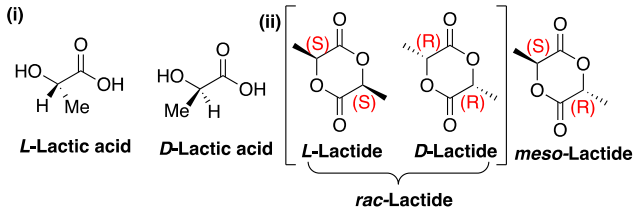


Figure 2. Stereoisomers of; (i) lactic acid and (ii) and lactide.[16,29,40]

1. *Isotactic:* A semi-crystalline material in which the stereochemical configuration between each repeating unit is preserved, for example -*RR- or* -*SS*-, thus ensuring all substituents occur on the same side of the polymer backbone. Isotactic PLA can be accessed through the ROP of pure *L*- and *D*-Lactide to afford PLLA and PDLA respectively, in the absence of epimerisation, the interconversion of stereocentres during polymerisation.

2. *Syndiotactic:* A semi-crystalline material that exhibits alternating stereochemical configuration between repeat units, for example -*SR*-. Consequently, substituents alternate between sides along the polymer backbone. Syndiotactic PLA can be produced from the ROP of *meso-Lactide.*

3. *Heterotactic:* A polymeric material characterised by doubly alternating stereochemical configuration within each repeating unit, giving rise to -*SSRR*- linkages, due to the preferential insertion of *L*- and *D*-monomer units.

4. *Atactic:* An amorphous material comprising of a completely random arrangement between stereogenic centres, thus imparting an absence of long range order.[41]

This intrinsic degree of crystallinity, and thus extent of intermolecular forces between chains, plays a crucial role in determining the material properties of the final polymer. Moreover, desirable high melting temperatures (T_m) can be attained through well-defined, high molecular weight control. As such, isotactic PLLA and PDLA homopolymers exhibits a high, well-defined melting point (T_m = 180 °C, Figure 3), owing to the presence of high regularity and crystallinity. These thermal temperatures can be improved further through combining PLLA and PDLA either as separate polymer chains or connected block co-polymers.[42,43] Such stereocomplexes can achieve a melting temperature of up to 230 °C depending on composition and molecular weight. The melting point of atactic PLA, however, remains undefined.[44]

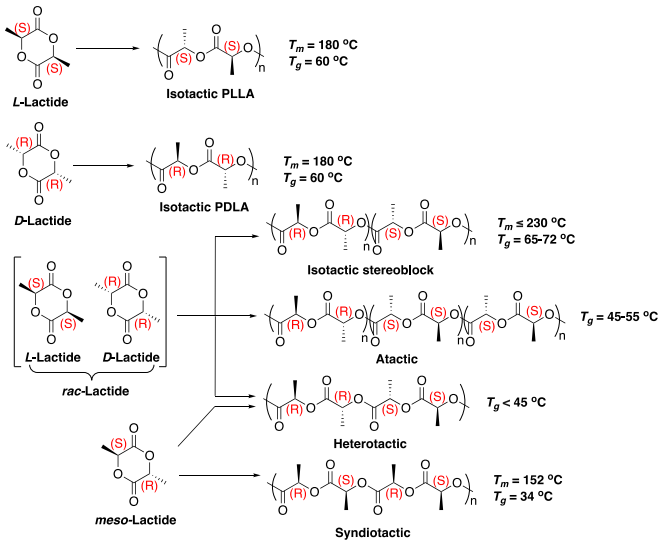


Figure 3. Possible stereochemical configurations of PLA from lactide polymerisation. Adapted from [32,45,46].

Another widely used parameter for characterising polymeric materials is the glass transition temperature (T_g).The T_g is defined as the temperature at which a polymer transitions from hard and brittle to a flexible, 'glassy' state.[41] T_g is dependent on both crystallinity and molecular weight, with isotactic PLA exhibiting the highest T_g, as seen in Figure 3 above. The ability to manipulate T_g, in conjunction with molecular weight and tacticity, enables the material properties of PLA to be engineered to the desired application, with isotactic PLA proving to be the most industrially attractive option.[15]

Stereoselectivity. Consequently, the stereoselective synthesis of PLA has attracted significant interest, with initiators based on a variety of different metals being reported in the literature, most commonly Al(III),[47–52] Mg(II),[53–57] Zn(II),[58–61] and group(IV).[62–66]

2.3 Catalyst Choice

Traditionally, industry employs $Sn(Oct)_2$ (Figure 4 below) as the catalyst of choice in the production of PLA, due to it being commercially available and inexpensive.[67,68] Moreover, $Sn(Oct)_2$ exhibits exceptional solubility in cyclic esters, ensuring a high catalyst activity in the ROP of lactide, which proceeds *via* the aforementioned coordination-insertion mechanism (Scheme 2).[69,70] However, Sn(II) hydroxides have been identified as harmful irritants, whilst potential Sn(IV) hydrolysis products are toxic. Additionally, the difficulty associated with completely removing trace Sn residues is a challenge routinely highlighted in the literature. [46,69,70] In light of these issues there is some debate in the literature regarding the suitability of this for certain biomedical applications.[69,70] There is therefore a clear desire for non-toxic and environmentally benign catalysts, which recent academic research has sought to address, with a particular focus on enhancing stereoselectivity whilst retaining high catalyst activity. However, whilst considerable research has focused on addressing this industry need in recent years, comparatively the fate of PLA waste, and plastics in general, has received markedly less attention in the literature. Herein, the focus of this perspective will now shift to exploring the various end-of-life (EOL) options currently available for PLA, in conjunction with potential future opportunities.

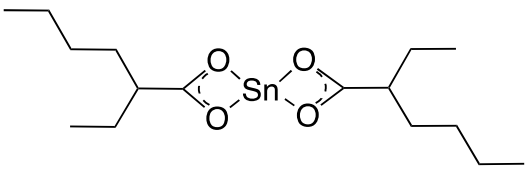


Figure 4. Chemical structure of tin(II) octanoate, $Sn(Oct)_2$, otherwise known as Sn(II)bis(2-ethylhexanoate).[69,70]

3.0 EOL Options of Plastics

Recent life cycle assessments (LCA) suggest PLA offers reductions of up to 40% in greenhouse gas (GHG) emissions and 25% in non-renewable energy use compared to traditional petrochemical-based plastics, including poly(ethylene) (PE) and poly(ethylene terephthalate) (PET), exemplifying PLAs green credentials.[4,71,72] However, societies transition towards a low-carbon and sustainable future will also require addressing a mounting waste crisis, particularly for plastics. Indeed, as of 2015, *ca.* 6300 Mtonnes of plastic waste has been generated.[73] Alarmingly, but unsurprisingly, 79% of this has accumulated in either landfill or the natural environment, whilst recycling and incineration accounted for 9% and 12% respectively. Moreover, ocean plastics have been subject to intense public scrutiny in recent years, with an estimated 4 to 12 Mtonnes of plastic waste produced on land entering the aquatic environment in 2010 alone.[73] It is clear that alternative plastic waste management systems are required to alleviate growing concerns, but first traditional methods will be discussed before exploring alternative routes tailored towards PLA.

3.1 Waste Management Strategies

Landfill. The conventional waste management approach employed, it is estimated 4900 Mtonnes, equating to 60% of all plastics ever produced, were discarded, collecting either in landfill or the natural environment.[73,74] In 2018, the UK government increased landfill tax in a bid to divert waste from limited landfill sites and encourage alternative waste management systems to be adopted.[75] Whilst immediate environmental impact is limited to collection and transport, long-term risks include local soil and groundwater contamination through pollutant and additive discharge upon waste degradation.[74,76] Moreover, non-biodegradable plastics persist for up to several decades.[76]

Incineration. An alternative waste management strategy, incineration reduces the need for landfill. Additionally, energy recovery can be achieved using a boiler prior to valorisation to either generate thermal or electrical energy. [76] This energy-recovery feature is an obvious benefit compared to landfill, where the plastic wastes intrinsic energy is lost to the surrounding environment. However, incineration is particularly sensitive to waste stream contamination. For example, Poly(vinyl chloride), (PVC), and halogenated additives are commonly found in mixed plastic waste, which are unsuitable for incineration due to the perceived risk of releasing halogenated pollutants into the environment. However, this can be remedied using sophisticated filters at the expense of increased capital. Furthermore, whilst there is potential for incineration to reduce emissions relative to landfill, the technology remains expensive, both in terms of CAPEX and maintenance, not to mention the inherent social limitations. Local communities often disfavour incineration facilities due to being unaesthetically pleasing and a source of local pollution.[74,76] In light of these challenges, incineration remains less prevalent compared to landfill as a waste management strategy.

Composting. A common feature of emerging bioplastics, as noted for PLA, biodegradability ensures composting as a viable alternative EOL option to the aforementioned strategies. Indeed, minimal environmental impact can be realised through careful consideration of the operating conditions and precautions undertaken. However, the composting conditions required are inherently complex, relying on a number of different factors, including humidity, ventilation and pH, which restrict its widespread use. As identified for incineration, composting is also sensitive to waste contamination. For example, PET entering the waste stream due to sorting mistakes will not degrade, rendering the compost of a lower quality. Moreover, research dedicated to improving the material properties of PLA often has an undesired negative impact on its compostability, resulting in slower degradation.[19,74,76,77] It is worth noting PLA composting typically takes between 6-12 weeks in the presence of microbes, requiring industrial composters operating between 50-70 ^{o}C.[78]

3.2 Linear Economy

Whilst the aforementioned waste management strategies offer alternative EOL options for plastics, crucially they each align with a linear economic model, (Figure 5). By convention, a linear economy involves extracting resources required to produce synthetic products, which at the end of their useful product life enter the waste stream, most likely accumulating in either landfill or the natural environment. Indeed, after a short first use cycle, 95% of all plastic packaging material, equating to *ca.* $ 80-120 billion, is lost annually to the current linear plastic economy, which at present fails to capture 32% of all plastic packaging using conventional collection systems.[5,79] It is therefore unsurprising that the linear economy is a significant contributor to the aforementioned plastic waste crisis, not only from an environmental perspective but economic too, costing $ 13 billion annually in damages to marine ecosystems alone.[79,80] Rather worryingly, plastic use is anticipated to double within the next 20 years, having increased 20-fold in the past 50 years.[5] To mitigate growing environmental concerns, whilst simultaneously facilitating an increase in plastic demand, it is imperative the polymer industry evolves, shifting its focus from single-use and disposable plastics to a model focussed on recapturing product value and reducing waste, namely the circular economy.[5,74,79]

3.3 Circular Economy

An alternative model to the linear economy, the circular economy (Figure 6) is based on 3 key principles:[1,5,79]

1. Reduce plastic waste and pollution through product design.
2. Retain resources and products in use.
3. Regenerate and preserve natural systems.

Presently, costs associated with after-use plastic externalities, in conjunction with associated GHG emissions, amount to a conservative estimate of $ 40 billion, exceeding the plastic packaging industries profit pool entirely.[5] A clear opportunity therefore exists for industry to adopt a new plastics economy, underpinned by the core principles of the circular economy, to enhance both socio-economic performance across the supply chain, whilst drastically reducing plastic waste, and with it the subsequent negative environmental impact. [1,5,79] Additional benefits include:

- Decoupling plastics from fossil fuels in exchange for renewable feedstocks, thus reducing societies dependency on depleting reserves.
- Recapturing material value from waste to prevent dematerialisation and reduce cycle losses. [5,79]

Figure 5. Flow diagram of linear economic model.[5,74,79]

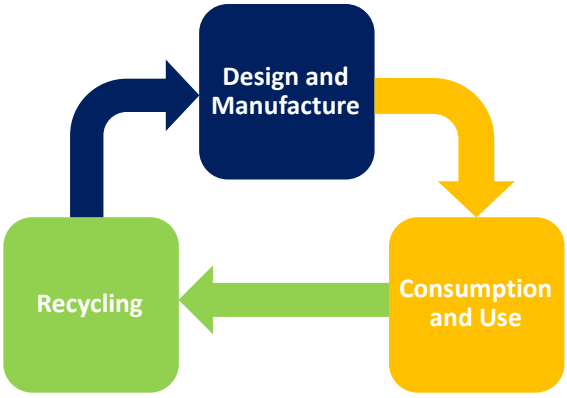


Figure 6. Flow diagram of circular economic model.[5,79]

However, at present, the majority of plastics are used for packaging and therefore designed with an anticipated life expectancy of less than 1 year, despite persisting in the environment for several decades following disposal. [5,6,74] Intuitively, this fatal design flaw, in combination with the linear economy, has been a major source of plastic waste, exemplified by the accumulation of ocean plastics. Alarmingly, it is estimated 150 Mtonnes of plastic waste resides in our oceans today, which is projected to increase to 250 Mtonnes by 2025 at current rates.[5,79,81,82] Whilst the plastics industry thus far has failed to operate proactively, instead resorting to reactive action, it is imperative future growth strives to resolve present-day challenges, whilst anticipating future needs and concerns. The emergence of the biopolymer industry signifies the industries intent to place sustainability at the core of its operations, which will undoubtedly play a crucial role in addressing the aforementioned challenges facing the industry today. Indeed, biodegradable plastics, such as PLA, can assist in reducing plastic waste accumulation in either landfill or the natural environment. However, following biodegradation any intrinsic value in the plastic waste is completely assimilated by the microorganisms, a major drawback compared to the circular economy which endeavours to recapture material value for reuse.

3.4 Waste Management Strategies for the Circular Economy

A major challenge therefore exists to develop alternative and targeted waste management strategies to promote the integration of biopolymers into the circular economy.[83] Traditionally, this is achieved through recycling.[5,79] For the purpose of this perspective, the recycling of plastic waste will be considered generally, but with a particular focus on PLA.

Mechanical Recycling. The mechanical recycling of plastic waste consists of remelting the material, either alone or in admixture with raw material, to produce granules or finished marketable products, such as bottles. Prior to remelting, the waste material is washed, dried, crystallised and then ground.

Mechanical recycling is often exploited in the reprocessing of PET, which is applicable to PLA. However, polymer thermomechanical degradation is often observed due to the high operating temperatures employed, resulting in a loss of its mechanical properties, rendering the polymer of lower quality relative to the starting material. Consequently, the polymer can be used in either less demanding applications, or alternatively mixed with raw material. Moreover, waste composition dictates the transformation temperature used, with incompatible plastic mixtures affording a final product with poorer mechanical properties.[74,76,84] The use of additives to retain or enhance polymeric properties following mechanical recycling have been reported in the literature, but at the expense of increased cost and additional raw starting material.[84] Whilst mechanical recycling offers promise as a short-term solution to recapturing value from waste, its limited number of cycles, and eventual material downgrading, renders the method unsuitable for retaining material value in the plastic economy in the long-term. There is therefore a pressing need to develop a portfolio of plastic waste management strategies to meet the diverse recycling demands of the circular economy, whilst simultaneously maintaining material market value. Furthermore, a 'one-method-treats-all' strategy is certainly unrealistic, owing to societies diverse material demands, and further accentuates the necessity to develop and diversify existing/future recycling technologies in order to realise a truly green, circular future.

Chemical Recycling. Otherwise known as feedstock recycling, chemical recycling involves exploiting a chemical process to either recapture the monomeric unit from plastic waste material, or directly convert it into other useful materials. This can be achieved through a number of different chemical processes, such as pyrolysis and catalysis. The advantages of chemical recycling compared to mechanical are three-fold:[74,76,84]

1. Obtain raw virgin starting materials, such as lactic acid, whilst preserving initial material properties.
2. Potential to produce value-added materials from waste feedstock.
3. Obviates the material downgrading prevalent in mechanical recycling, thus ensuring material value is retained within the plastic economy indefinitely.

Whilst the technology has long been established, its application has previously been limited by high plant and process costs relative to cheap petrochemical feedstocks.[74] However, the polymer industries expressed interest in shifting to a circular economy approach, in conjunction with policy and legislation, will undoubtedly play a crucial role in accelerating the uptake of such technology. Furthermore, a recent study by Piemonte *et al*.[85] demonstrated the production of lactic acid from chemical recycling to be less energy intensive compared to the initial glucose fermentation, thus making it attractive from both an economic and environmental. Moreover, in 2014, Europe and China reported recycling rates of 30% and 25% respectively. Comparatively, the US has been steadily underperforming with a 9% recycling

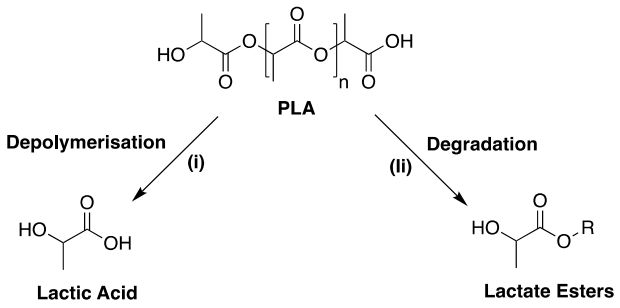
rate since 2012.[73] The US therefore represents a significant market that could potentially greatly benefit from alternative waste management strategies, along with Europe and China.

4.0 Chemical Recycling of PLA

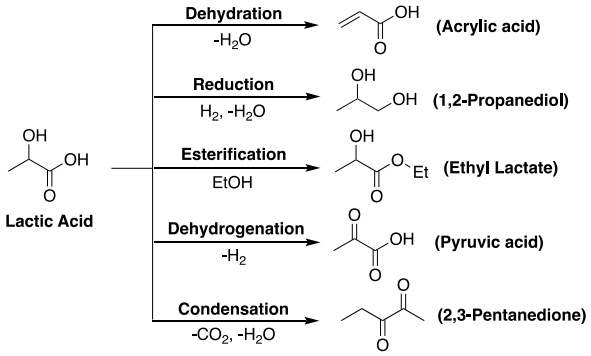
The chemical recycling of PLA has attracted increasing interest in recent years owing to its potential to further integrate PLA into a circular economy. Presently, the chemical recycling options available for PLA can be characterised into two distinct routes, namely depolymerisation or degradation, as seen in (Scheme 4). Although the terms depolymerisation and degradation are often used interchangeably, it is important to recognise there is a distinct technical difference. The depolymerisation of PLA involves recapturing the monomeric unit, either lactic acid or lactide, whilst degradation involves the transformation of PLA waste into reusable resources, ideally value-added materials, such as lactate esters (Scheme 4).

4.1 Depolymerisation of PLA.

In recent years, research into the depolymerisation of PLA has garnered significant interest in the literature for a number of reasons. First, lactic acid has been identified as a future platform chemical by the US Department of Energy, with its chemical versatility enabling a plethora of commodity chemicals to be accessed, as seen in Scheme 5 below.[40,86] Second, lactic acid will undoubtedly play a crucial role in attaining a low carbon future, which will be underpinned by a bio-based circular economy, with production projected to increase annually by 5-8%.[87]



Scheme 4. Chemical recycling options for PLA: (i) depolymerisation or (ii) degradation.



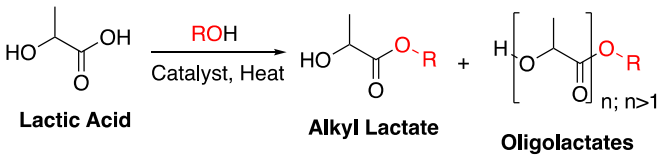
Scheme 5. Select example of possible lactic acid conversion pathways into useful commodity chemicals. Adapted from[40].

Research into the depolymerisation of PLA waste therefore has the potential to complement traditional methods to satisfy this anticipated increase in demand, whilst simultaneously alleviating food chain competition concerns associated with sourcing lactic acid from biomass, not to mention the obvious environmental benefits. As such, a number of depolymerisation methods have been reported in the literature. Traditionally, the depolymerisation of PLA in industry is achieved through hydrolysis, operating under elevated temperatures (100-250 °C) comparable to those used in the PET industry. Moreover, a strong inorganic acid catalyst, typically H_2SO_4 or HNO_3, is also commonly employed, due to the enhanced rate of reaction resulting in reduced residence times.[15] More recently, Coszach *et al*.[76] also achieved the hydrolysis of PLA to lactic acid, both with and without NaOH, with the latter negating the need for harsh and highly corrosive reagents. Hydrolysis was achieved between 80-180 °C, with pressures of up to 10 bar. Additionally, superior PLA dissolution and polymer separation was realised with alkyl lactates as the solvent of choice. Classically, higher operating temperatures and pressures are conceded in the absence of harsh acid/base catalysts. Hirao *et al*.[88,89] achieved 90% conversion to *L*-lactic acid from PLLA within a 10-20 minute hydrolysis period (PLLA:H_2O = 1:20) at 250 °C under high pressure. Superior depolymerisation was then observed under microwave irradiation, achieving 45% conversion to *L*-lactic acid after 120 minutes (PLLA:H_2O = 1:3), compared to 800 minutes under conventional heating. However, there is uncertainty surrounding the viability of upscaling microwave technology. These conventional heating findings were consistent with previous pioneering work done by Tsuji *et al*.,[90] with both depolymerisation methods operating under melt conditions, removing the need for potentially expensive solvents, which are traditionally a source of significant waste in industry.[15] Moreover, the depolymerisation of PLA films/scaffolds also remains an active area of research, which is typically achieved using NaOH or HCl, as seen in work done by Odelius *et al*.[91] In light of these developments, it is clear an opportunity still exists to further optimise these systems, especially from an operational standpoint. There is therefore an underlying demand for sustainable and environmentally benign catalyst alternatives to reduce depolymerisation energy intensity, thus making it more environmentally friendly, whilst preserving process efficiency. Within

the last few decade, enzymes have been identified as a potential candidate,[92–95] although their industrial application remains limited by possible scalability issues.[96,97] Whilst the depolymerisation of PLA is one possible circular economy approach, with the recovery of the lactic acid monomer unit offering a base towards preparation of valuable commodity chemicals a better approach would be the direct preparation of such chemicals. Therefore, degradation can promote an enhanced economic performance. For this reason, PLA degradation has attracted increasing interest in the literature in recent years.

4.2 Degradation of PLA.

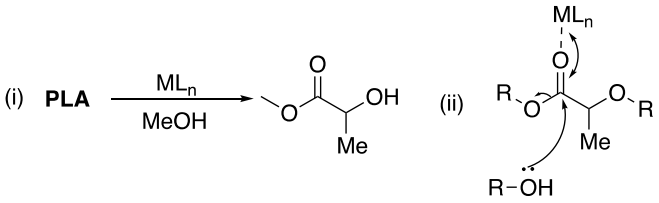
A number of degradation methods for PLA have been reported in the literature. One possible route is thermal degradation, whereby PLA is converted into a number of different possible products, such as acetaldehyde or lactide, depending on the system employed.[98–102] However, such systems are characterised by high operating temperatures (200 – 400 °C), rendering the process both energy intensive and expensive to operate. To mitigate these factors, attention has shifted towards developing robust and highly active catalyst systems. In particular, research concerning the production of lactate esters from PLA has gathered appreciable momentum in the last 10 years. Low molecular weight lactate esters have been cited as potential green solvent substitutes for conventional hydrocarbon-based solvents, owing to their biodegradability and low toxicity, not to mention their low vapour pressure, which makes them both safer and easier to handle.[103,104] Indeed, their possible applications are far reaching, from the agriculture and polymer industry through to pharmaceuticals and paint formulations.[105,106] Moreover, in 2012, the market price of ethyl lactate was $2 per lb compared to $1 per lb for commodity PLA, thus there is potential for lactate esters to deliver additional value into the PLA supply chain.[107] Indeed, lactate esters can be converted into either lactic acid or lactide, further promoting a circular economy.[86] Traditionally, lactate ester synthesis relies either on protection group strategies to prevent the formation of oligolactate by-products (Scheme 6), stoichiometric quantities of catalyst or long reaction times at high temperatures, rendering such methods both resource and energy intensive.[103] More recently, the metal-mediated alcoholysis of lactide has been shown to effectively yield alkyl lactates,[108,109] however this is potentially a less desirable use of a direct PLA precursor. Presently, DuPont possess a patent for the transformation of PLA to various lactate esters (R = Me, Et and ^{n}Bu) using 2-3 equivalents of ROH per polymer unit in the presence of an acid catalyst, namely H_2SO_4, achieving between 69-87% within 2 h between 150 – 190 °C, under reactant autogenic pressure.[110] Since H_2SO_4 is both highly corrosive and toxic, attention in the literature has shifted towards developing more environmentally benign alternatives. Song and co-workers demonstrated the first use of ionic liquids (ILs), including [Bmim][Ac] and [HSO_3-pmim][HSO_4], in the methanolysis of PLA.[111,112] However, whilst ILs present a green alternative to H_2SO_4, offering both superior catalyst activity and product separation, their inherent high cost and intrinsic viscosity presents possible scalability issues.



Scheme 6. Direct transformation of lactic acid to alkyl lactates (lactate esters) *via* a transesterification reaction. An excess of ROH is required to achieve high lactate ester conversion, with the liberation of H_2O negatively influencing both the reaction equilibrium and inhibiting self-esterification under sustained heating. Since lactic acid bears both hydroxyl and carboxylic acid end groups, intermolecular esterification is possible, giving rise to oligolactate by-products. Adapted from [103].

Organocatalysts such as 4-(dimethylamino)pyridine (DMAP) and 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) have also been shown by Nederberg *et al.*[113] and Leibfarth *et al.*[107] respectively to be feasible catalysts in PLA degradation. Indeed, the latter exhibited remarkable activity, achieving > 90% ethyl lactate yield at room temperature using 3 equivalents of EtOH per ester group in the presence of 1 mol% TBD. Certainly, the ability to achieve such high conversions under ambient conditions is of considerable interest to industry, both from an economic and environmental perspective, though TBD is limited by properties akin to H_2SO_4.[114] By comparison, examples of PLA degradation mediated by metal-based catalysts in the literature are scarce (Scheme 7). Jones and co-workers reported the relatively mild methanolysis of commercial, high M_n PLA to methyl lactate (Me-LA) at both 25 and 80 °C in the presence of Zr(IV)/Hf(IV)-Salalen complexes.[115] Interestingly, degradation proceeded irrespective of polymer tacticity, observing 75% conversion to Me-LA within 24h at room temperature. However, complexity associated with the ligand preparation limits the large-scale viability of these catalysts. Liu *et al.*[112] recently reported a contrasting study investigating the methanolysis of PLA using a series of simple, commercially available metal-based catalysts. $FeCl_3$ was identified as the outstanding candidate, achieving 87% conversion to Me-LA within 4h at 130 °C using 1 mol% $FeCl_3$ and a 5:1 of n_{MeOH}:n_{PLA}. Moreover, $FeCl_3$ could be recycled up to 6 times before any appreciable decrease in catalyst activity and selectivity was observed. The method reported therefore has the potential to overcome numerous limitations associated with conventional methods, most notably unfeasible catalyst recovery and equipment corrosion. However, there is obvious scope to further develop these ligand systems, with the aim of retaining comparable activity, but under significantly milder conditions akin to those previously reported.[107,115] Most recently, Roman-Ramirez *et al.*[116] reported the degradation of various gradings of PLA to Me-LA using a Zn-Imino monophenolate complex. Me-LA conversion was shown to be dependent on both temperature and catalyst loading, consistent with the literature, achieving up to 100% Me-LA within 1h at 90 °C using

2 mol% catalyst and 7:1 of n(MeOH):n(ester) in THF. Indeed, Me-LA formation was observed at temperatures as low as 40 °C using 1 mol% catalyst, albeit only 17% conversion.



Scheme 7. (i) Degradation of PLA to methyl lactate (Me-LA), (ii) General mechanism for acid catalysed transesterification reaction. Interestingly, the metal centre(M)-carbonyl oxygen(O) interaction is analogous to that highlighted in the coordination-insertion mechanism depicted in Scheme 2, implying catalysts active for PLA production may also be active in degradation.

Fliedel *et al.*[117] have also reported a PLA degradation system based on Zn, more specifically a binuclear Zn(II) N-Heterocyclic carbene complex. Low molecular weight PLLA was degraded, achieving up to 28% Me-LA after 24h at room temperature further demonstrating the utility of zinc based systems. Recent work by Petrus *et al.* provides further incentive for investigating metal-based systems, particularly from an environmental and economic standpoint. A range of lactate esters were prepared from a number of different alcohols, both in the absence and presence of metal-based catalysts. Reaction temperatures up to 260 °C were observed for the former, whilst the latter enabled temperatures as low as 80 °C to be accessed. Finally, it is important to highlight the aforementioned studies considered waste composed exclusively of PLA. In reality, mixed plastic waste, arising due to sorting mistakes, is more industrially representative, but at present the effect of this on both catalyst activity and product separation remains poorly understood. Work done by Sanchéz *et al.*[118] remains one of the few examples of selective plastic recycling in the literature to date. The selective degradation of PLA to Me-LA from a PLA-PET waste mixture was achieved using $Zn(OAc)_2$. The inherent non-reactivity of PET under identical reaction conditions was exploited, enabling solid PET to be separated by filtration post reaction. It was also recommended that the residual zinc be removed post processing to prevent further reaction with Me-LA, to form a Zn-Lactate ester intermediate, or prevent interference during subsequent steps. It is imperative selective degradation receives greater consideration in the literature to overcome initial industrial inertia to adoption and increase relevance of academic reports to industrial conditions. Recently, steps other than esterification reactions have been explored in the literature. Catalysts based on rare earth metals, including ruthenium and iridium, have been shown to be active in the reduction of a range of polyesters.[119–121] For PLA, the typical product of hydrogenation is propane-1,2-diol and quantitative conversion is typically observed. Westhues *et al* also demonstrate the selective degradation of PLA/PET mixtures through judicial choice of

temperature.[122] While the scarcity, and therefore high cost, of such precious metals is a limitation of such systems, particularly from a scalability and sustainability perspective, these examples highlight the versatility of products that can potentially be generated from chemical degradation.

5.0 Conclusions

Growing environmental concerns associated with the accumulation of plastic waste in the natural environment has incentivised extensive research into renewable alternatives. As such, PLA has emerged as one of the outstanding candidates within the last 20 years owing to its green credentials. Consequently, considerable research has focused on the development of environmentally benign and sustainable catalyst alternatives to $Sn(Oct)_2$ for PLA production, with a particular focus on stereoselectivity in recent years. Comparatively, research concerning the EOL options for PLA waste, and plastics generally, remains significantly less well explored. Indeed, conventional waste management strategies for plastics align with a linear economic model, which is a primary contributor to the aforementioned waste crisis. There is therefore a clear industry appetite to shift towards a circular economic model to reduce plastic waste, whilst simultaneously retaining material value, which will require the development of alternative waste management strategies. One possible method is mechanical recycling, but the technology remains limited by eventual material downgrading arising due to thermomechanical degradation, forcing material repurposing to less noble applications. A promising alternative to this method is chemical recycling, which encompasses both the depolymerisation and degradation of PLA, with the latter enabling value-added materials, such as lactate esters, to be accessed. This in turn will provide additional value to the PLA supply chain, thus promoting enhanced economic performance, a particularly attractive feature to industry. Additionally, there is the potential for lactate esters to be used as green solvent substitutes, negating the need for potentially expensive and environmentally harmful hydrocarbon-based solvents. This promise of superior economic and environmental performance will undoubtedly play a crucial role in overcoming inevitable barriers to adoption in industry. However, traditionally such materials are resource and energy intensive to produce, relying either on expensive and/or highly corrosive reagents, harsh operating conditions or long reaction times, limiting their scalability. There is therefore a clear opportunity to optimise these systems, especially from an operational standpoint, with metal-based catalysts a possible solution, though literature examples remain scarce. As such, an opportunity exists to develop industrially viable, robust catalyst systems based on earth-abundant metals and scalable ligands for PLA degradation. Indeed, functionally versatile ligand systems, such as Schiff-base complexes, will enable such catalysts to be fine-tuned towards PLA degradation. However, challenges remain surrounding catalyst recovery, whilst the impact of mixed plastic waste on catalyst activity and product separation remains poorly understood. Looking forward, policy and legislation will play a crucial role in accelerating the uptake and implementation of such technology.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

We would like to thank the EPSRC for funding (EP/L016354/1) for a PhD studentship to JP and (EP/P0164051/1) for a PDRA for PM.

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